



A review on solid oxide derived from waste shells as catalyst for biodiesel production

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ABSTRACT

The waste eggs and mollusk shells are found to be the richest sources of calcium carbonate and have been utilized for various purposes after proper treatments. When calcined at a proper temperature calcium carbonate converts into CaO, which is a metal oxide. Researchers have found that the CaO prepared from the waste shells can be used as catalyst in biodiesel production process. Utilization of waste shells as a source of CaO not only gives an opportunity to use it as catalyst but also adds value to the waste generated. In this paper a brief discussion with recent development on biodiesel production using waste shell derived solid oxide as catalyst is presented.

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1. Introduction

Many recent research programs based on energy sector are focused on the development of concepts such as renewable resources, sustainable development, green energy and eco-friendly process [1]. Increasing world population and industrial development have all led to serious energy crisis and global warming. It is, therefore necessary to develop ecologically clean and safe energy technologies for a sustainable future.

“Oil from the sun” has been envisaged as fuel since the very beginning of automotive transportation. In 1911, for the first time, Rudolph Diesel used peanut oil to run the diesel engine invented by him owing to which different varieties of edible and non edible oil have been studied for the purpose. The interest in energy self sufficiency and periodic petroleum shortages spurred research into vegetable oil as a petroleum diesel substitute. It is known that vegetable oil was investigated as diesel fuel during the energy crisis of the 1970–1980s and were also used as emergency fuels during World War II. The different feedstocks that were investigated for biodiesel production includes palm oil, soybean oil, rapeseed oil, cottonseed oil, castor oil, Jatropha oil, etc. In some cases, investigations were also carried out on non vegetable sources such as

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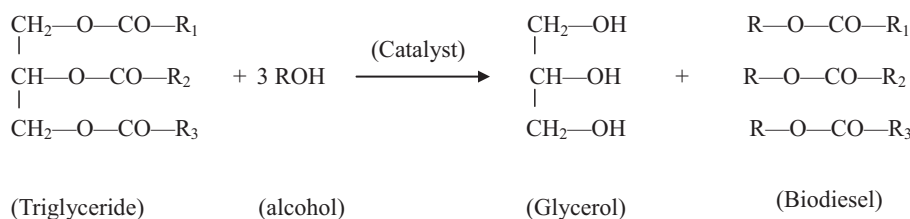
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Table 1
Methods of production of biodiesel.

Methods	Definition	Advantage	Disadvantage	References
Pyrolysis or thermal cracking	Method of conversion of one substance into another by application of heat with the aid of the catalyst in the absence of air or oxygen	1. Lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility 2. The final products are similar to diesel fuel in composition	Energy intensive	[64]
Micro-emulsions	A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles	1. Fuel viscosity is lowered 2. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles	Lower cetane number and energy content	[65]
Direct use and blending	Either use vegetable oil directly or is blended with diesel	Liquid nature and portability Heat content (~80% of diesel fuel) readily available; renewability	(1) Higher viscosity (2) Lower volatility (3) The reactivity of unsaturated hydrocarbon chains	[66]
Transesterification	Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol	Renewability; higher cetane number; lower emissions; higher combustion efficiency	Glycerol disposal and waste water problem	[67]

animal fats and waste cooking oil. The major problem associated with vegetable oil is its high viscosity which leads to poor atomization of the fuel in the engine's combustion chamber and results in operational problem such as engine deposit. The most appropriate way to adjust the viscosity of the vegetable oil and animal fats for use in unmodified diesel engines is by converting the triacylglyceride into lower molecular weight fatty acid monoalkyl ester standardized as biodiesel when meeting the requirement of ASTM D 6751 and EN 14214 [2–4]. Chemically biodiesel is mono alkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils and animal fats [3]. It can be used in its neat form or as a blend with conventional diesel fuel in diesel engine without any modification and can reduce the particulate emissions from engine [4].

There are four methods which have been investigated to reduce the viscosity of vegetable oil namely, pyrolysis, dilution with conventional petroleum-derived diesel fuel, micro-emulsification and transesterification. Table 1 presents an overview of these methods in biodiesel production. Among all these methods transesterification process has been widely used to reduce the high viscosity of triglycerides and produce biodiesel with higher cetane number. Transesterification is the process in which the vegetable oil/animal fat is subjected to chemical reaction with alcohol in presence of a catalyst to form glycerol and ester [5,6]. The simplified form of this chemical reaction is presented as:



where R_1, R_2, R_3 are the fatty acid chains.

Transesterification is mainly affected by the methanol and oil molar ratio – which is used to drive the reaction towards forward direction, catalyst – which is depended on the amount of free fatty acid present in the vegetable oil/animal fat, reaction temperature and reaction time. Generally, the biodiesel production via transesterification can be catalyzed in four basic routes viz. base-catalyzed,

direct acid catalyzed, enzyme catalyzed and non catalytic transesterification using methanol or methanol with a co-solvent [7].

Among the different routes mentioned, the preferred method is the base-catalyzed transesterification of vegetable oils with simple alcohol where one can achieve high purity and yield of biodiesel product within a short time (30–60 min) [8]. A schematic representation of alkali-catalyzed transesterification is presented in Fig. 1 [9]. Even though homogeneous catalyzed biodiesel production processes are relatively faster and show high conversions, their utilization in vegetable oil transesterification results in soap formation which is an undesirable side-reaction [10]. Besides that, they cannot be reused or regenerated, since the catalyst is consumed in the reaction which makes the separation of catalyst from products very difficult requiring more equipment resulting in higher production costs [11]. Because of the problems associated with the use of homogeneous catalysts, there has been an increasing development of new catalysts for biodiesel production [12].

Biodiesel synthesis using heterogeneous catalyst in lieu of homogeneous catalyst could potentially lead to cheaper production costs by enabling reuse of the catalyst and opportunities to operate in a fixed bed continuous process [13]. The use of heterogeneous catalytic system in the transesterification of triglyceride also implies the elimination of several washing steps [14]. A variety of solid catalysts have been examined for the

transesterification reaction and new catalysts are continued to be reported in the literature. Most of these catalysts belong to either acid or base catalytic systems. This includes calcium oxide [15], calcium ethoxide [16], CaTiO_3 , CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaZrO_3 , and CaO—CeO_2 [17], Li—CaO [18], Heteropoly acids [19], metal-loaded MgAl [20], zirconia-supported Isopoly and Heteropoly tungstates

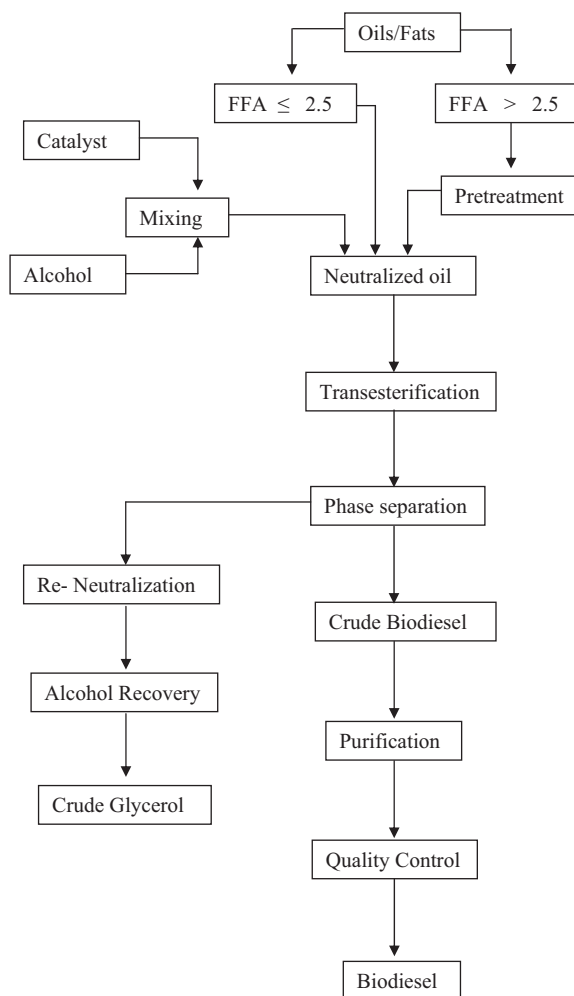


Fig. 1. Simplified process flow chart of alkali-catalyzed biodiesel production.

[21], MgO-loaded KOH [22], alumina/silica supported K_2CO_3 [23], etc. A brief list of some of the heterogeneous catalysts used for transesterification along with their preparation conditions is presented in Table 2. The preparation methods of these catalysts are time consuming and the catalysts are also not environmentally benign. Though, most of the heterogeneous catalysts prepared can be reused again but at one particular point their lifetime reaches at minimum and finally stops showing no activity. These catalysts also create disposal problems and add to environment pollution.

Recently, research interest has been grown in the production of biodiesel using waste mollusk shells and eggs shells as catalysts. Pioneering work done by Wei et al. [24] in the transesterification of vegetable oil with egg shell as heterogeneous catalyst has suggested an easy way of “green” catalyst synthesis. Based on this study different researchers have also proposed the utility of industrial waste shell as catalyst not only for biodiesel production but also in other fields of catalysis. Shrimp Shells [25], shells of golden apple snail and meretrix venus [26] are some of the examples which have been successfully used by the researchers as heterogeneous catalysts for biodiesel production. It is reported that these catalysts can be reused, are environmental friendly and at the same time add value to the recycled waste. The aim of this paper is to review and discuss the literature regarding the use of different waste shells for biodiesel production via transesterification of vegetable oil.

2. Components of waste shells

Research on the shell structure of mollusks and egg shells began quite early. Researchers proposed models for the purpose and had used various techniques to come to a conclusion. This section presents a brief overview of the investigation taken up regarding the major constituents of the mollusk as well as egg shells.

2.1. Mollusk shell

Research on molluska shell is not new rather it dated back to 17th century with the initial studies based on molluscs anatomy [27]. The investigation of mollusk shell microstructures, built of complex calcite and/or aragonite layer intergrowths, is of interest in many fields of science [28]. It is known that many invertebrates produce hard skeletons made of crystallized biogenic materials to protect and support their soft bodies [29]. The molluscan shell biomineralization involves the uptake of the mineral ions from the environment and their assembly into a functional organic matrix secreted by specialized cells of the outer mantle epithelium [30]. Mollusk shells are a natural ceramic composite with excellent fracture strength and fracture toughness, which are attributed to their unique microstructures. The shell material is composed of 95–99% crystalline calcite or aragonite (form of calcium carbonate, $CaCO_3$) and protein film which are used as the binder in varying amount from 0.1% to 5% by weight [28].

A molluscan shell can be divided into three primary sections: the outer layer is called as periostracum and mainly composed of conchiolins, the middle layer is known as prismatic layer consisting of oriented calcitic crystals and finally the nacreous layer

Table 2

Preparation and reaction conditions of different heterogeneous catalyst in the transesterification of different oil feedstock.

Catalyst	Feedstock	Preparation conditions			Reaction conditions		Conversion (C)	Reference
		Method	Calcination temperature (°C)	Methanol:oil ratio	Reaction temperature (°C)	Reaction time (h)		
TiO_2 -MgO	Waste cooking oil	Sol-gel	500–700	30:1	150	6	92.3 (Y)	[68]
CaMgO, CaZnO	Jatropha curcas oil	Coprecipitation method	800 and 900	15:1	65	6	80%< (C)	[69]
KF/Eu ₂ O ₃	Rapeseed oil	Precipitation method	600	12:1	Methanol reflux temperature	1	92.5% (C)	[70]
Ca(OCH ₂ CH ₃) ₂	Soybean oil	–	Dried in oven at 105	12:1	65	1.5	95.0 (Y)	[71]
Eu(NO ₃) ₃ /Al ₂ O ₃	Soybean oil	Impregnation	300–900	6:1	70	6	63 (C)	[72]
Lithium-doped ZnO	Soybean oil	Impregnation	500	12:1	65	3	96.3 (C)	[73]
KF/ZnO	Soybean oil	Impregnation	500	10:1	65	9	87 (C)	[74]
Na doped SiO ₂	Jatropha oil	Sol-gel	600	15:1	65	45	99 (C)	[75]

which contains aragonite crystals. In 1930, Bøggild laid the foundation for all subsequent studies of molluscan shell structure in a classic paper in which he defined different types of structure and surveyed their distribution, and that of aragonite and calcite mineralogies, among the mollusca [31]. The presence of shell organics was reported by French researcher Fremy who named it conchiolin. Crenshaw discovered soluble shell organic matrices and postulated the presence of sulphated polysaccharides as a nucleation factor [32,33]. The importance of sulphated sugars and acidic proteins was demonstrated in an experiment of acidic analysis on soluble shell organics. The result obtained indicated that acidic macromolecules were the key player in the nucleation of calcium carbonate. The acidic macromolecules recognized were acidic proteins and sulphated sugars [34,35]. Early studies carried out on conchiferan shell proteins were mainly focused on Asx and Glx. This research generally overestimated the acidity of those proteins and such analysis could not reveal the actual percentage of aspartic acid and glutamic acid in the shell [36]. Studies carried out with 2 D gel electrophoresis on the calcitic prismatic layer of *Pinctada margaritifera* and *Pinna nobilis* [37], the entire aragonitic shells of *Nautilus marcomphalus*, *Spirula spirula*, and *Sepia* sp. [38], and the nacre layer of *Unio pictorum* [39] showed the presence of acidic protein as one of their constituents. Weiner et al. [34,35] studied the insoluble shell organic matrices by using X-ray/electron diffraction in which it was revealed that chitin was present in the shell matrix. At the same time it was stated that the amount of chitin might differ with different mollusk shell or it may not be present in some mollusk shell. Chitin is a linear homopolymer consisting of β -(1-4)-linked N-acetyl-D-glucosamine subunits and according to some researchers it is one of those biopolymers identified in the organic parts of the mollusk shells which play an important role in the crystal orientation of mollusk shells. Levi-Kalisman et al. [40] proposed that the interlamellar sheets in the shells were mainly composed of highly ordered and aligned β -chitin fibrils with little or no evidence for silk-like proteins. Weiss and Schönlitzer [41] characterized chitin during the larval shell development by using confocal laser scanning microscopy. In their investigation they reported that biomineralisation of mollusk shells was highly influenced by chitin on various levels of hierarchy.

2.2. Egg shells

Eggshell is a bioceramic composite which consists of a mineral part containing 95% calcite aggregates pervaded with an organic matrix resulting in a structure which has excellent mechanical properties [42]. The chicken eggshell comprises calcified shell and shell membranes including inner and outer membranes. These membranes retain albumen and prevent penetration of bacteria. Shell membranes are also essential for the formation of eggshell [43] which not only protect the contents of the egg from mechanical impacts but also form microbacterial invasions like *Salmonella*. They also control the exchange of water and gases through the pores during the extrauterine development of the chick embryo [44]. It also acts as a source of nutrient, primarily calcium, to the developing embryo.

During the initial research on the composition of the chicken egg shells, Burley and Vadehra [45] suggested that the organic matter of egg shell and the shell membrane mainly contain protein along with carbohydrate and lipids in small amounts. It was also reported by Bronsch and Diamantstein [46] that the egg shells also contained uronic acid which affected the breaking strength of the shell. Further investigations on chicken egg shell have revealed that the chicken egg shells are mainly composed of calcium carbonate along with some traces of magnesium carbonate, phosphate, sodium, potassium, carbon, zinc, manganese, iron and copper. In the elemental composition of eggshell, it has been reported that

the major element is calcium and its amount is about 98.2% in the shell. The other elemental compositions are 0.9% magnesium and 0.9% phosphorus (present in shell as phosphate) [47].

3. Waste shell in biodiesel production

3.1. Mollusk shell waste catalyst

Oyster is one of the dominant products of shell fish farms in some countries like Korea and Japan but the oyster shells are the unwanted waste product from mariculture and present a major disposal problem. This waste generated has not only affected the environment but also the ecosystem resources. It produces nasty smell as a consequence of the decay of flesh remnant attached to oyster or the microbial decomposition of salts into gases such as NH_3 , H_2S and Amine [48]. Therefore conversion of the waste oyster shells to a beneficial and economically viable product can solve the problem partially, if not fully. Kwon et al. [49] used the waste oyster shells as an effective reagent for phosphorous removal from waste waters. They found that the shells contained mainly calcium carbonate but when it was heated at higher temperatures of 750–800 °C, it was converted to calcium oxide. CaO formation was confirmed by XRD patterns obtained from the study. In another experiment, Chae et al. [50] recycled the oyster waste shells by treating it with plasma pyrolysis technique. These experiments showed that the oyster shells were mainly composed of CaCO_3 but when heated to certain temperatures lead to the formation of single metal oxide-CaO. This conclusion helped Nakatani et al. [51] to employ combusted oyster shell for transesterification. They combusted the waste oyster shells at different temperatures of 100, 500, 700, 800, 900 and 1000 °C for 3 h and found that the XRD patterns obtained for the combusted oyster shells at and above 700 °C were identical to those of CaO. They applied factorial design and response surface methodology to optimize the reaction conditions. It was observed that the most important factor affecting the biodiesel purity was the reaction time and catalyst concentration. From the second order model, the optimum reaction conditions of catalyst concentration and reaction time was found to be 25 wt% and 5 h, respectively. They claimed that the oyster shell combusted at higher temperatures could be reused as catalyst for biodiesel production and the yield obtained was comparable to that of CaO. Boro et al. [52] investigated the performance of *Turbonilla striatula* shells as catalyst in the transesterification of mustard oil. They observed that catalyst calcination temperature is the most important factor affecting the transesterification process. It was reported that the catalyst calcined above 800 °C showed better catalytic activity than those calcined at lower temperature. This was attributed to the formation of CaO at higher calcination temperature. The catalyst was deactivated after repeated use and its initial catalytic activity could be regained by calcining the recovered catalyst at 800 °C. Studies were also conducted on the waste mollusk shells of golden apple snail shell and meretrix venus shell by Viriya-empikul et al. [26] in the transesterification of palm olein oil. They calcined the shell at 800 °C for 4 h and reported the formation of CaO at a temperature above 800 °C. Though both the catalysts acts as a heterogeneous basic catalyst it was observed that better yield of 95% was obtained with golden apple snail shell. Apart from surface area and amount of Ca content present in the catalyst the catalytic activity was also influenced by the catalyst calcination temperature and methanol to oil molar ratio. However reusability studies of the catalysts were not investigated which is an important aspect of a heterogeneous catalyst.

Another popular seafood is Mud crab (*Scylla serrata*) which is farmed on a commercial scale in tropical countries but again in this case also the shell of mud crab is treated as waste. Boey et al. [53] investigated the use of waste shells of mud crab as catalyst

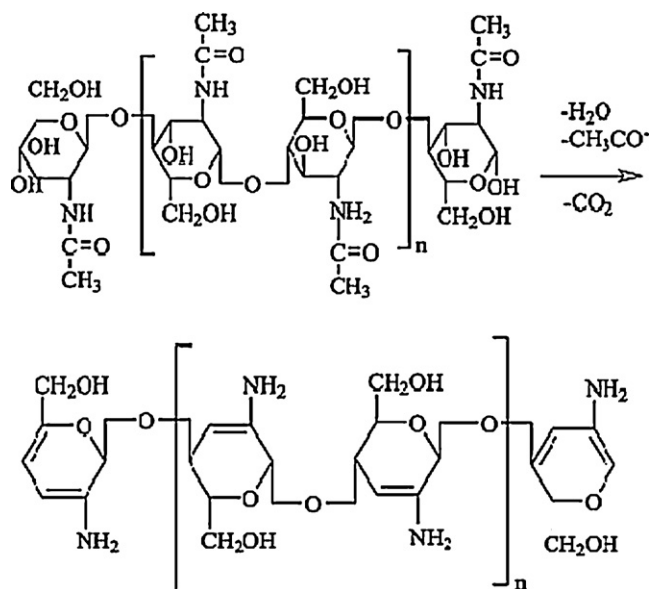


Fig. 2. The transformation of chitin molecules during the incompletely carbonization process.

for transesterification and compared its performance with laboratory grade CaO. For better understanding of the various variables affecting the reaction, they also conducted statistical analysis using a Central Composite Design. According to the statistical analysis the best fit model was observed to be the quadratic model which identified catalyst concentration as the most important parameter for biodiesel purity followed by reaction temperature and methanol to oil ratio. All the factors affecting transesterification were depended on each other and it was impossible to obtain minimum purity at the lowest level of any one factor. However minimum biodiesel purity of 95.6% could be achieved at higher (+1) or centre levels (0) of different factors with the proposed catalyst. A big advantage of the calcined catalyst was reported in terms of its reusability as it could be reused for 11 times without much drop in its activity. Similar studies were also conducted in the optimization of reaction variables in the transesterification of chicken fats with the combined waste shells of crab and cockle. They reported that under the optimal condition of 4.9 wt% catalyst amount and 0.55:1 methanol to oil mass ratio, above 98% methyl esters conversion was achieved. The authors also concluded from their study that different waste containing CaO could be combined to produce methyl esters [54]. Yang et al. [25] prepared shrimp shell catalyst through a tristep route in which initially the shrimp shells were incompletely carbonized, loaded with KF followed by calcination. The major constituent of the shrimp shells is chitin which occupies 69% of the dry weight of the shrimp shell. During incomplete carbonization small molecules present in the shell were evaporated and water was eliminated from the chitin molecules leading to the formation of a stereo polymer composed of six-member heterocyclic compounds with increased surface area (Fig. 2) called as quasiaromatic compounds. The incompletely carbonized shells were loaded with KF which act as a modifier and during activation active sites were formed by the reaction of the shells with KF. The authors reported that the catalytic activity of the catalyst proposed was highly influenced by the carbonization temperature, KF loading and activation temperature. Detailed study revealed the optimum preparation condition as carbonization temperature at 450 °C, 25 wt% KF loading and activation temperature at 250 °C. Under these optimum preparation conditions, the conversion reached to 89.1% when the reaction was carried out at 65 °C with a catalyst amount 2.5 wt%, a methanol/rapeseed oil molar ratio 9:1 for a reaction time of 3 h.

Reusability studies for the same catalyst showed a drop in catalytic activity which was attributed to the loss of active sites due to covering by the resultant. The catalyst has an advantage that it could be regenerated by treating it in soxhlet's apparatus with petroleum ether as solvent for 3 h. In a similar experiment carried out by Xie et al. [55] biont shell catalyst were prepared by incomplete carbonization followed by impregnation with KF. The high activity of the catalyst was attributed to the formation of active sites during the reaction between incompletely carbonized chitin and KF. In addition the weak polar nature of the biont shell was found to prevent reverse glycerolysis reaction which ultimately contributes to the high catalytic activity.

3.2. Egg shell

We have already discussed in our previous section that the chicken egg shells are mainly composed of calcium carbonate and along with some traces of magnesium carbonate, phosphate, sodium, potassium, carbon, zinc, manganese, iron and copper [43]. Recycling industrial by-products and ecological manufacture procedures have also prompted the research into waste egg shell. Development of value-added by-products from this waste is of great interest as eggs are part of daily meal in most of the countries. Investigations related to the utilization of the egg shell as a renewable catalyst was taken up by many scientists in different work. Montilla et al. [56] used egg shells as catalyst to produce lactulose from milk ultrafiltrate as source of lactose. Some other researchers have used egg shells for preparing dielectric material and zeolite type A [57,58], as a support for immobilizing a variety of enzymes and in CH₄ reforming [59,60]. Detailed studies related to the effect of temperature on the X-ray diffraction (XRD), infrared (IR) and ESR spectra of chicken egg shell in the temperature range 298–1173 K were conducted by Engin et al. [61]. They confirmed that the egg shells were mainly composed of calcites and upon heating at higher temperature it got converted into CaO. This confirmation was a matter of interest for researchers who used these shells as catalyst in the transesterification reaction.

Wei et al. [24] introduced egg shells as catalyst in the methanolysis of soybean oil. The shells were initially washed and dried followed by calcination at a temperature range of (200–1000 °C) for 2 h. They observed that upon calcination the morphology of the shell remained the same till calcination at 600 °C and the changes in the shell structure started to appear at 700 °C. Calcination above 800 °C reduced the particle size and the particle shape became more irregular. This was attributed to the changes in the composition of the shell upon calcination. XRD patterns obtained for shells calcined at different temperatures revealed that the shells calcined below 700 °C contained CaCO₃ as a major constituent and peaks of CaO started to appear at higher calcination temperature. Furthermore the biodiesel yield was also found to be in accordance with the calcination temperature. The yield was found to be maximum for shell calcined above 800 °C. They also studied the effect of methanol/oil ratio, catalyst amount and reaction time on biodiesel production. Under the optimum condition of 9:1 molar ratio of methanol to oil, 3 wt% egg shells calcined at 1000 °C, reaction temperature of 65 °C biodiesel yield of 95% was obtained when the reaction was carried out for 3 h. Viriya-empikul et al. [26] also observed the same XRD patterns for the calcined egg shells as Wei et al. In the reaction carried out with palm olein oil as raw material they observed that the biodiesel yield was 95% after a reaction time of 2 h. They reported that the yield increased with an increasing methanol to oil ratio and the optimum methanol to oil ratio in their study was 12:1. Egg shell catalyst exhibited a high surface area with small particle size which was concluded to be the reason behind the high yield obtained during the study. Sharma et al. [62] used chicken egg shells for the transesterification of Karanja oil. They reported that

the initial weight loss for the calcined catalyst occurred at around 400–480 °C which was attributed to the decomposition of $\text{Ca}(\text{OH})_2$. The next weight loss observed at 700 °C was due to the decomposition of calcium carbonate along with the loss of some inorganic impurities. Upon calculation of the particle size it was found that the particle size of the uncalcined catalyst was larger than the calcined catalyst. This decreased in particle size during calcination resulted in decreasing crystallinity of the catalyst. It was attributed to the presence of water in CaO. However the XRD patterns of the calcined shells confirmed the formation of calcium oxide at higher calcination temperature. They found that optimum catalyst used for the best yield was 2.5% whereas it was 3.0% in the case of Wei et al. [24]. They found that a reaction time of 2.5 h was found to be best suited for the biodiesel yield of 95% and reaction beyond that time did not increased the yield of biodiesel.

4. Mechanism of CaO catalyzed reaction

As discussed in previous sections, the waste shells are mainly composed of calcium carbonate and the formation of CaO during different catalyst preparation methods acts as the main driving force behind transesterification process for biodiesel production. Experiments have also been carried out by taking manufactured CaO for biodiesel production. Detailed study on the mechanism of manufactured CaO was carried out by Kawashima et al. [15] and Lim et al. [63] and the proposed mechanism for CaO during transesterification is as follows:

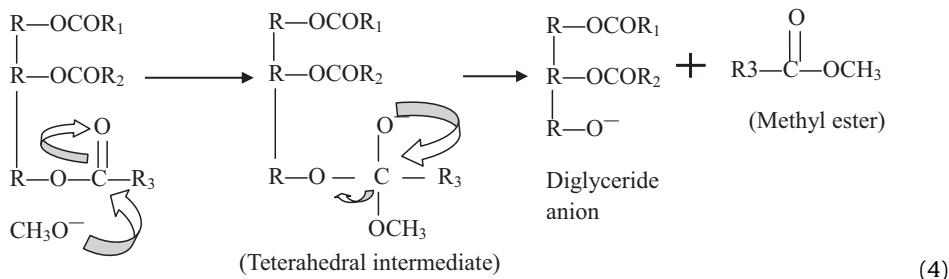
Step 1: Dissociation of CaO and methanol while activation of the catalyst (Eqs. (1) and (2)).



Step 2: Methanol and hydroxide ion reacts to form methoxide anion (Eq. (3)).



Step 3: Carbonyl carbon of triglyceride is attacked by the methoxide anion formed in the previous reaction to form tetrahedral intermediate. This is followed by the rearrangement of the intermediate molecule to form methyl ester and diglyceride (Eq. (4)).



Step 4: The methoxide anion attack on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. This continues till a total of three moles of methyl esters and a mole of glycerol is formed during the reaction.

5. Conclusion

Transesterification reaction is highly influenced by the reaction conditions, catalyst used, molar ratio of methanol to oil. The catalyst synthesized with the waste shells opens door for renewable catalyst and at the same time recycles the waste generated. The various shells that have been employed have proved that highly active and reusable solid catalysts can be prepared with no time

loss by just calcining the shells. Utilization of these waste materials not only reduces the catalyst cost but also promotes environmentally benign process. These shells may also find their utility in other base catalyzed important organic reactions which will add value to the waste generated.

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